

AN INVESTIGATION OF THE INFLUENCE
OF IMPURITIES ON THE DISSOCIATION
OF GASES IN THE ELECTRODE-LESS
DISCHARGE

BY
CHARLES ROLAND EDDY
Sc. B., Brown University, 1935

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY IN CHEMISTRY IN THE
GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1938

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INTRODUCTION

Although a vast amount of work has been done on the properties and reactions of atomic hydrogen during the last decade, most of the workers have been content with studying the reactions of a complex mixture containing a small percentage of hydrogen atoms, and relatively little attention has been focused on the development of a better source of atoms. Because of the unreliability of the electrode-less discharge when excited by a spark-gap oscillator, most researchers in this field have been driven to the long discharge tube with electrodes, which has the disadvantage of metal from the electrodes sputtering into other parts of the system where it catalyzes recombination of the atoms and may react with other gases present.

The purpose of the present research was two-fold: (1) to perfect the electrode-less discharge technique so that its practicability, reproducibility, efficiency, and available power can compare favorably with the use of electrode tubes, (2) to find a relatively inert gas which can be added to hydrogen in small quantities and produce high yields of hydrogen atoms, thus avoiding the use of water vapor or the anti-catalytic wall coatings often used.

VACUUM-TUBE OSCILLATOR

A five-kilowatt vacuum-tube oscillator was constructed to supply the radio-frequency power for exciting the electrode-less discharge, using a type HM-207 vacuum-tube made in our own machine shop from the designs of Sloan, Thornton, and Jenkins¹. This was a water-cooled metal tube using wax

glass-to-metal seals and continuously evacuated by a glass expanding-nozzle dibutyl-phthalate vapor diffusion pump so constructed that there was a straight vertical path from the interior of the vacuum tube to the pump nozzle through a length of 70 millimeter diameter tubing, the only obstruction being an internal liquid-air cooled trap so constructed as to offer very little resistance to the gas flow yet prevent a molecule from getting through in a straight line. This pump was supported by another dibutyl-phthalate pump and a Cenco-Megavac rotary pump, the two diffusion pumps having internally heated boilers as designed by Bearden².

The oscillator circuit was of the Hartley type operating on approximately 30 meters. Its tank coil was eleven 4-inch turns of $\frac{5}{16}$ " copper tubing water-cooled, its tank condenser was a special high-voltage type designed by Green and Kruger³ and of the same dimensions as theirs, its plate blocking condenser was a 6" x 18" Pyrex cylinder $\frac{3}{16}$ " thick wrapped inside and out with aluminum foil⁴, its grid-leak was a 20,000 ohm wire-wound resistor capable of dissipating 400 watts, and its grid condenser was three 3" square copper sheets sandwiched between four Pyrex glass plates 4" square and 4 mm. thick. The plate power was supplied by a 5KVA 12,000 volt transformer, using the vacuum-tube as its own rectifier.

This vacuum-tube oscillator was capable of producing electrode-less discharges over a pressure range of from .005 mm. to 40 mm. of mercury, with uniform, reproducible results and with sufficient power and stability to do all that the long electrode discharge tube is capable of doing, without the disadvantages of the latter.

EXPERIMENTAL

The oscillator was used to study electrode-less discharges in hydrogen in the neighborhood of .05 mm. with special emphasis on the percentage of hydrogen atoms produced, the atoms being measured by a continuous-flow calorimetric

method⁵ whereby the atoms strike silver foil on the outside of a copper tube where they recombine and liberate heat to a stream of water flowing through the tube, the number of atoms being determined from the temperature rise of the water. This method is superior to former systems of measuring hydrogen atoms since it is not subject to pressure limitations and is capable of continuous readings over indefinite periods of time.

Tests on hydrogen saturated with water vapor at room temperature yielded dissociations up to 80% which declined sharply during each run, thus confirming the observations on the electrode discharge by Poole⁵ and demonstrating that the phenomena are not a property of the electrode discharge but also apply to the electrode-less discharge. By plotting the logarithm of the dissociation against time and obtaining straight lines, it was shown that the dissociation obeys an equation of the type

$$d = d_0 e^{-at}$$

where d is the dissociation at time t , d_0 is the dissociation when the discharge was started, and a is a constant that is approximately the same for each run.

Tests on pure, dry, oxygen-free hydrogen yielded dissociations up to 20%, although past workers have not reported appreciable dissociations of dry hydrogen. Blank test runs on hydrogen standing static in the system and on pure argon flowing as before revealed negligible temperature rises in the calorimeter, thus proving that the observed dissociations of dry hydrogen are not errors in the system of measurement. It is thought that the cause of the dissociation lies in the increased power available from the vacuum-tube oscillator or possibly in the higher frequency. Tests were also made on mixtures of dry hydrogen with from 1 to 10% of argon and of nitrogen, which were found not to affect appreciably the dissociation of the hydrogen.

SUMMARY

A vacuum-tube oscillator has been developed that has sufficient power and reproducibility to replace the usual spark-gap oscillator for excitation of the electrode-less discharge and thereby make the electrode-less discharge supersede in practicability the long electrode discharge tube as a source of hydrogen atoms.

While a gas has not yet been discovered that will greatly increase the dissociation of hydrogen, the 20% dissociations produced in dry hydrogen by this oscillator may become a valuable method for the study of reactions of atomic hydrogen when not in the presence of water vapor, since much can be learned about atomic hydrogen from dissociations of only 20%, much of the past work having been done with percentages no greater than this.

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VITA

The author was born in Providence, Rhode Island, on August 31, 1914. He obtained his elementary training in the public schools of East Providence and graduated from East Providence High School in June, 1931. He entered Brown University in 1931 and in 1935 received the degree of Bachelor of Science in Chemistry, Summa Cum Laude. From 1935 to 1938 the author did graduate work at the University of Illinois. He held a teaching assistantship in the Chemistry Department during the school year 1935-1936 and a University fellowship during the school years 1936-1937 and 1937-1938. He is a member of Phi Lambda Upsilon, Phi Beta Kappa, and Sigma Xi.

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